Analytical Methods

Cyanide

9010B/9013/9014

METHOD 9010B

TOTAL AND AMENABLE CYANIDE: DISTILLATION

1.0 SCOPE AND APPLICATION

1.1 Method 9010 is reflux-distillation procedure used to extract soluble cyanide salts and many insoluble cyanide complexes from wastes and leachates. It is based on the decomposition of nearly all cyanides by a reflux distillation procedure using a strong acid and a magnesium catalyst. Cyanide, in the form of hydrocyanic acid (HCN) is purged from the sample and captured into an alkaline scrubber solution. The concentration of cyanide in the scrubber solution is then determined by Method 9014 or Method 9213. Method 9010 may be used as a reflux-distillation procedure for both total cyanide and cyanide amenable to chlorination. The "reactive" cyanide content of a waste, that is, the cyanide content that could generate toxic fumes when exposed to mild acidic conditions, is not determined by this method. Refer to Chapter Seven of SW-846 for the additional information on reactive cyanide.

1.2 This method was designed to address the problem of "trace" analyses (<1000 ppm). The method may also be used for "minor" (1000 ppm - 10,000 ppm) and "major" (>10,000 ppm) analyses by adapting the appropriate sample dilution. However, the amount of sodium hydroxide in the standards and the sample analyzed must be the same.

2.0 SUMMARY OF METHOD

2.1 The cyanide, as hydrocyanic acid (HCN), is released from samples containing cyanide by means of a reflux-distillation operation under acidic conditions and absorbed in a scrubber containing sodium hydroxide solution. The cyanide concentration in the absorbing solution is then determined colorimetrically or titrametrically by Method 9014 or by ion-selective electrode by Method 9213.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure. Chlorine and sulfide are interferences in Method 9010.

3.2 Oxidizing agents such as chlorine decompose most cyanides. Chlorine interferences can be removed by adding an excess of sodium arsenite to the waste prior to preservation and storage of the sample to reduce the chlorine to chloride which does not interfere.

3.3 Sulfide interference can be removed by adding an excess of bismuth nitrate to the waste (to precipitate the sulfide) before distillation. Samples that contain hydrogen sulfide, metal sulfides, or other compounds that may produce hydrogen sulfide during the distillation should be treated by the addition of bismuth nitrate.

3.4 High results may be obtained for samples that contain nitrate and/or nitrite. During the distillation, nitrate and nitrite will form nitrous acid, which will react with some organic compounds to form oximes. These compounds once formed will decompose under test conditions to generate HCN. The possibility of interference of nitrate and nitrite is eliminated by pretreatment with sulfamic acid just before distillation. Nitrate and nitrite are interferences when present at levels higher than 10 mg/L and in conjunction with certain organic compounds.

3.5 Thiocyanate is reported to be an interference when present at very high levels. Levels of 10 mg/L were not found to interfere.

3.6 Fatty acids, detergents, surfactants, and other compounds may cause foaming during the distillation when they are present in high concentrations and may make the endpoint for the titrimetric determination difficult to detect. Refer to Sec. 6.8 for an extraction procedure to eliminate this interference.

4.0 APPARATUS AND MATERIALS

4.1 Reflux distillation apparatus such as shown in Figure 1 or Figure 2. The boiling flask should be of one liter size with inlet tube and provision for condenser. The gas scrubber may be a 270-mL Fisher-Milligan scrubber (Fisher, Part No. 07-513) or equivalent. The reflux apparatus may be a Wheaton 377160 distillation unit or equivalent.

4.2 Hot plate stirrer/heating mantle.

4.3 pH meter.

4.4 Amber light.

4.5 Vacuum source.

4.6 Refrigerator.

4.7 Erlenmeyer flask - 500 mL.

4.8 KI starch paper.

4.9 Class A volumetric flasks-1000,250, and 100 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for sample collection, preservation, and handling

5.3.1 Sodium arsenite (0.1N), $NaAsO_2$. Dissolve 3.2 g $NaAsO_2$ in 250 mL water.

5.3.2 Ascorbic acid, $C_6H_8O_6$.

5.3.3 Sodium hydroxide solution (50%), NaOH. Commercially available.

5.3.4 Acetic acid (1.6M) CH_3COOH. Dilute one part of concentrated acetic acid with 9 parts of water.

5.3.5 2,2,4-Trimethylpentane, C_8H_{10}.

5.3.6 Hexane, C_6H_{14}.

5.3.7 Chloroform, $CHCl_3$.

5.4 Reagents for cyanides amenable to chlorination

5.4.1 Calcium hypochlorite solution (0.35M), $Ca(OCl)_2$. Combine 5 g of calcium hypochlorite and 100 mL of water. Shake before using.

5.4.2 Sodium hydroxide solution (1.25N), NaOH. Dissolve 50 g of NaOH in 1 liter of water.

5.4.3 Sodium arsenite (O.1N). See Section 5.3.1.

5.4.4 Potassium iodide starch paper.

5.5 Reagents for distillation

5.5.1 Sodium hydroxide (1.25N). See Section 5.4.2.

5.5.2 Bismuth nitrate (0.062M), $Bi(NO)_3 \cdot 5H_2O$. Dissolve 30 g $Bi(NO)_3 \cdot 5H_2O$ in 100 mL of water. While stirring, add 250 mL of glacial acetic acid, CH_3COOH. Stir until dissolved and dilute to 1 liter with water.

5.5.3 Sulfamic acid (0.4N), H_2NSO_3H. Dissolve 40 g H_2NSO_3H in 1 liter of water.

5.5.4 Sulfuric acid (18N), H_2SO_4. Slowly and carefully add 500 mL of concentrated H_2SO_4 to 500 mL of water.

5.5.5 Magnesium chloride solution (2.5M), $MgCl_2 \cdot 6H_2O$. Dissolve 510 g of $MgCl_2 \cdot 6H_2O$ in 1 liter of water.

5.5.6 Lead acetate paper.

5.5.7 Stock potassium cyanide solutions - Refer to Method 9014 for the preparation of stock cyanide solutions and calibration standards.

6.0 SAMPLE COLLECTION, PRESERVATION AND HANDLING

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Chapter Nine.

6.2 Samples should be collected in plastic or glass containers. All containers must be thoroughly cleaned and rinsed.

6.3 Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with potassium iodide-starch test paper. A blue color indicates the need for treatment. Add 0.1N sodium arsenite solution a few mL at a time until a drop of sample produces no color on the indicator paper. Add an additional 5 mL of sodium arsenite solution for each liter of sample. Ascorbic acid can be used as an alternative although it is not as effective as arsenite. Add a few crystals of ascorbic acid at a time until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 g of ascorbic acid for each liter of sample volume.

6.4 Aqueous samples must be preserved by adding 50% sodium hydroxide until the pH is greater than or equal to 12 at the time of collection.

6.5 Samples should be chilled to 4°C.

6.6 When properly preserved, cyanide samples can be stored for up to 14 days prior to sample preparation steps.

6.7 Solid and oily wastes may be extracted prior to analysis by method 9013. It uses a dilute NaOH solution (pH = 12) as the extractant. This yields extractable cyanide.

6.8 If fatty acids, detergents, and surfactants are a problem, they may be extracted using the following procedure. Acidify the sample with acetic acid (1.6M) to pH 6.0 to 7.0.

CAUTION: This procedure can produce lethal HCN gas.

Extract with isooctane, hexane, or chloroform (preference in order named) with solvent volume equal to 20% of the sample volume. One extraction is usually adequate to reduce the compounds below the interference level. Avoid multiple extractions or a long contact time at low pH in order to keep the loss of HCN at a minimum. When the extraction is completed, immediately raise the pH of the sample to above 12 with 50% NaOH solution.

7.0 PROCEDURE

7.1 Pretreatment for cyanides amenable to chlorination

7.1.1 This test must be performed under amber light. $K_3[Fe(CN)_6]$ may decompose under UV light and hence will test positive for cyanide amenable to chlorination if exposed to fluorescent lighting or sunlight. Two identical sample aliquots are required to determine cyanides amenable to chlorination.

7.1.2 To one 500 mL sample or to a sample diluted to 500 mL, add calcium hypochlorite solution dropwise while agitating and maintaining the pH between 11 and 12 with 1.25N sodium hydroxide until an excess of chlorine is present as indicated by KI-starch paper turning blue. The sample will be subjected to alkaline chlorination by this step.

CAUTION: The initial reaction product of alkaline chlorination is the very toxic gas cyanogen chloride; therefore, it is necessary that this reaction be performed in a hood.

7.1.3 Test for excess chlorine with KI-starch paper and maintain this excess for one hour with continuous agitation. A distinct blue color on the test paper indicates a sufficient chlorine level. If necessary, add additional calcium hypochlorite solution.

7.1.4 After one hour, add 1 mL portions of 0.1N sodium arsenite until KI-starch paper shows no residual chlorine. Add 5 mL of excess sodium arsenite to ensure the presence of excess reducing agent.

7.1.5 Analyze the total cyanide concentration of both the chlorinated and the unchlorinated samples by Method 9014 or 9213. The difference between the total cyanide concentration in the chlorinated and unchlorinated samples is equal to the cyanide amenable to chlorination.

7.2 Distillation Procedure

7.2.1 Place 500 mL of sample, or sample diluted to 500 mL in the one liter boiling flask. Pipet 50 mL of 1.25N sodium hydroxide into the gas scrubber. If the apparatus in Figure 1 is used, add water until the spiral is covered. Connect the boiling flask, condenser, gas scrubber and vacuum trap.

7.2.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately two bubbles of air per second enter the boiling flask through the air inlet tube.

7.2.3 If samples are known or suspected to contain sulfide, add 50 mL of 0.062M bismuth nitrate solution through the air inlet tube. Mix for three minutes. Use lead acetate paper to check the sample for the presence of sulfide. A positive test is indicated by a black color on the paper.

7.2.4 If samples are known or suspected to contain nitrate or nitrite, or if bismuth nitrate was added to the sample, add 50 mL of 0.4N sulfamic acid solution through the air inlet tube. Mix for three minutes.

Note: Excessive use of sulfamic acid could create method bias.

7.2.5 Slowly add 50 mL of 18N sulfuric acid through the air inlet tube. Rinse the tube with water and allow the airflow to mix the flask contents for three minutes. Add 20 mL of 2.5M magnesium chloride through the air inlet and wash the inlet tube with a stream of water.

7.2.6 Heat the solution to boiling. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, and closing the vacuum source, disconnect the gas scrubber.

7.2.7 Transfer the solution from the scrubber into a 250-mL volumetric flask. Rinse the scrubber into the volumetric flask. Dilute to volume with water.

7.2.8 Proceed to the cyanide determinative methods given in Methods 9014 or 9213. If the distillates are not analyzed immediately, they should be stored at 4°C in tightly sealed flasks.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Employ a minimum of one reagent blank per analytical batch or one in every 20 samples to determine if contamination or any memory effects are occurring.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Run one replicate sample for every 20 samples. A replicate sample is a sample brought through the entire sample preparation and analytical process. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Run one matrix spiked sample every 20 samples to check the efficiency of sample distillation by adding cyanide from the working standard or intermediate standard to 500 mL of sample to ensure a concentration of approximately 40 µg/L. The matrix spiked sample is brought through the entire sample preparation and analytical process.

8.6 It is recommended that at least two standards (a high and a low) be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. If distilled standards do not agree within ± 10% of the undistilled standards, the analyst should find the cause of the apparent error before proceeding.

8.7 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were ± 0.005 to ± 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

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FIGURE 1.
APPARATUS FOR CYANIDE DISTILLATION

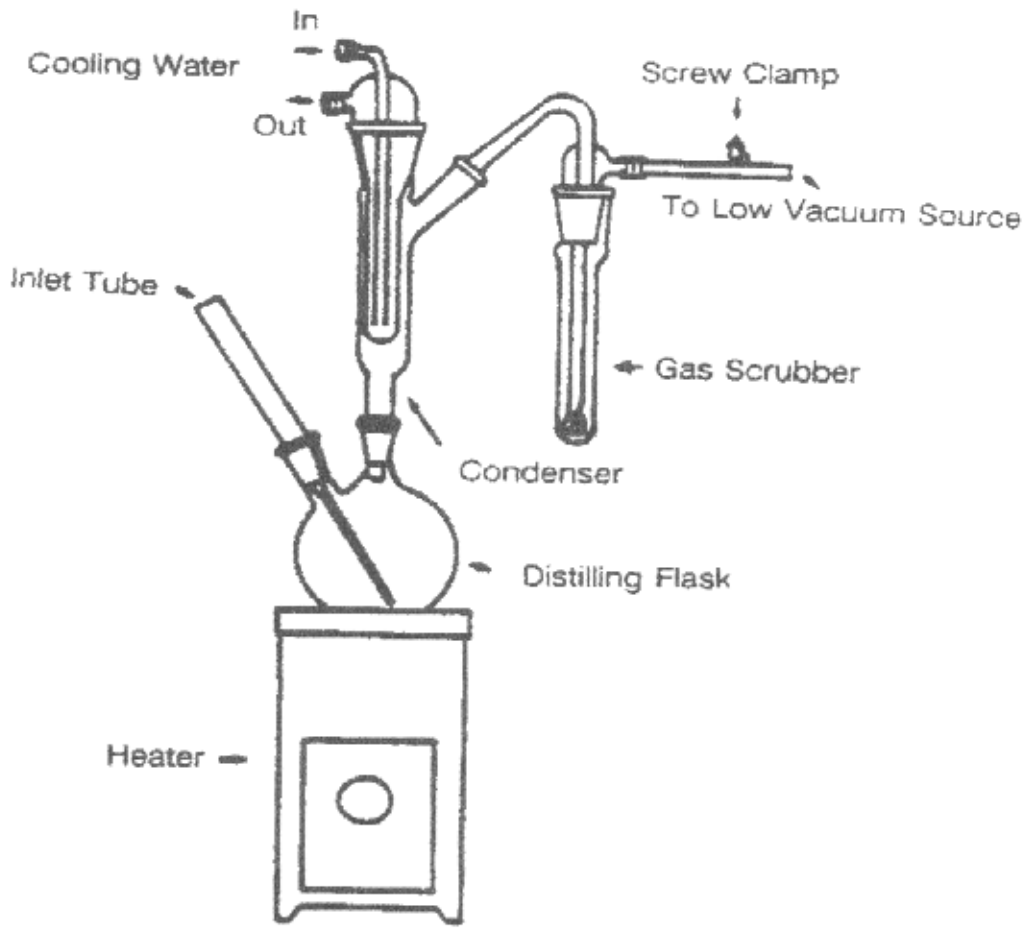
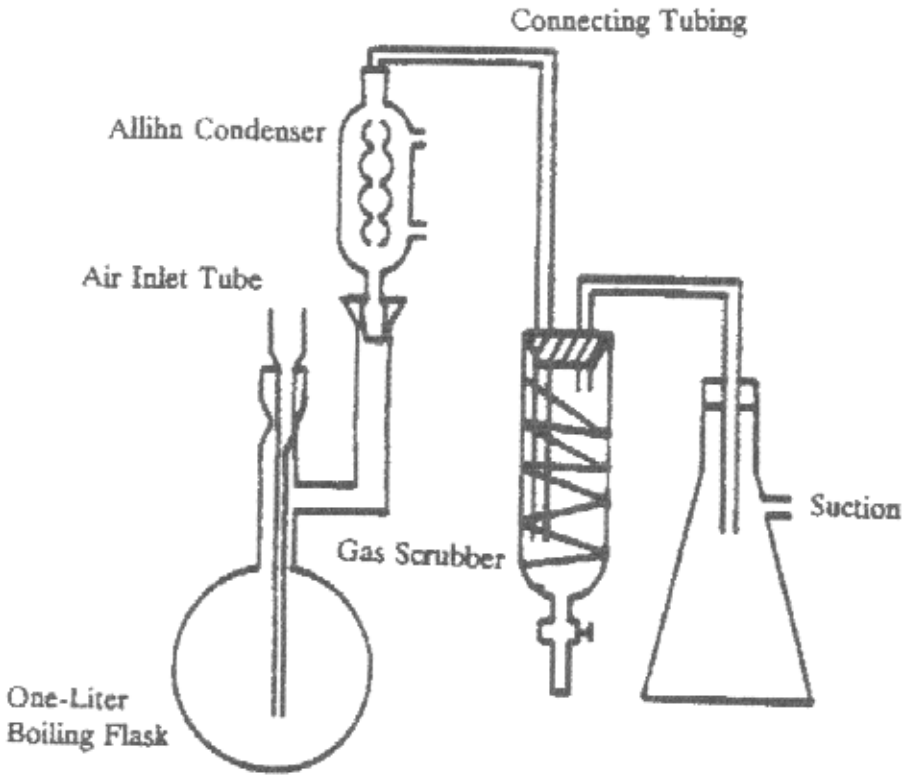
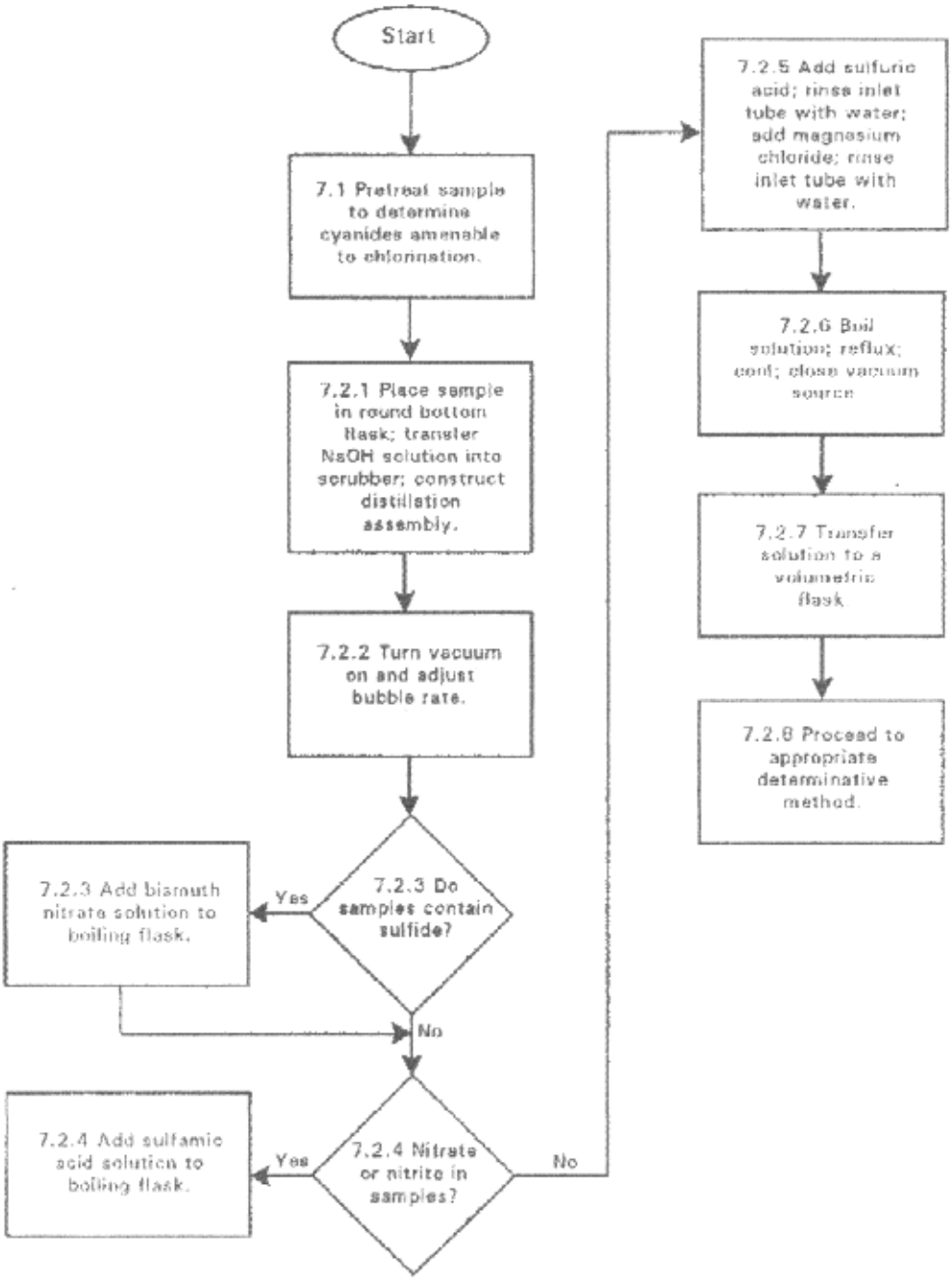


FIGURE 2.
APPARATUS FOR CYANIDE DISTILLATION



TOTAL AND AMENABLE CYANIDE: DISTILLATION



METHOD 9013
(APPENDIX TO METHOD 9010)

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS

1.0 SCOPE AND APPLICATION

1.1 The extraction procedure described in this method is designed for the extraction of soluble cyanides from solid and oil wastes. The method is applicable to oil, solid, and multiphasic samples. This method is not applicable to samples containing insoluble cyanide compounds.

2.0 SUMMARY OF METHOD

2.1 If the waste sample contains so much solid, or solids of such a size as to interfere with agitation and homogenization of the sample mixture in the distillation flask, or so much oil or grease as to interfere with the formation of a homogeneous emulsion, the sample may be extracted with water at pH 10 or greater, and the extract distilled and analyzed by Method 9010. Samples that contain free water are filtered and separated into an aqueous component and a combined oil and solid component. The nonaqueous component may then be extracted, and an aliquot of the extract combined with an aliquot of the filtrate in proportion to the composition of the sample. Alternatively, the components may be analyzed separately, and cyanide levels reported for each component. However, if the sample solids are known to contain sufficient levels of cyanide (about 50 µg/g) as to be well above the limit of detection, the extraction step may be deleted and the solids analyzed directly by Method 9010. This can be accomplished by diluting a small aliquot of the waste solid (1-10 g) in 500 mL water in the distillation flask and suspending the slurry during distillation with a magnetic stir-bar.

3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in Method 9010.

4.0 APPARATUS AND MATERIALS

4.1 Extractor - Any suitable device that sufficiently agitates a sealed container of one liter volume or greater. For the purpose of this analysis, agitation is sufficient when:

1. All sample surfaces are continuously brought into contact with extraction fluid, and

2. The agitation prevents stratification of the sample and fluid.

4.2 Buchner funnel apparatus

4.2.1 Buchner funnel - 500-mL capacity, with 1-liter vacuum filtration flask.

4.2.2 Glass wool - Suitable for filtering, 0.8 μm diameter such as Corning Pyrex 3950.

4.2.3 Vacuum source - Preferably a water driven aspirator. A valve or stopcock to release vacuum is required.

4.3 Top-loading balance - capable of weighing 0.1 g.

4.4 Separatory funnels - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Sodium hydroxide (50% w/v), NaOH. Commercially available.

5.4 n-Hexane, C_6H_{14}.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must be collected using a plan that addresses the considerations discussed in Chapter 4 of this manual. See Section 6.0 of Method 9010 for additional guidance.

7.0 PROCEDURE

7.1 If the waste does not contain any free aqueous phase, go to Step 7.5. If the sample is a homogeneous fluid or slurry that does not separate or settle in the distillation flask when using a Teflon coated magnetic stirring bar but mixes so that the solids are entirely suspended, then the sample may be analyzed by Method 9010 without an extraction step.

7.2 Assemble Buchner funnel apparatus. Unroll glass filtering fiber and fold the fiber over itself several times to make a pad about 1 cm thick when lightly compressed. Cut the pad to fit the Buchner funnel. Weigh the pad, then place it in the funnel. Turn the aspirator on and wet the pad with a known amount of water.

7.3 Transfer the sample to the Buchner funnel in small aliquots, first decanting the fluid. Rinse the sample container with known amounts of water and add the rinses to the Buchner funnel. When no free water remains in the funnel, slowly open the stopcock to allow air to enter the vacuum flask. A small amount of sediment may have passed through the glass fiber pad. This will not interfere with the analysis.

7.4 Transfer the solid and the glass fiber pad to a tared weighing dish. Since most greases and oils will not pass through the fiber pad, solids, oils, and greases will be extracted together. If the filtrate includes an oil phase, transfer the filtrate to a separatory funnel. Collect and measure the volume of the aqueous phase. Transfer the oil phase to the weighing dish with the solid.

7.5 Weigh the dish containing solid, oil (if any), and filter pad. Subtract the weight of the dry filter pad. Calculate the net volume of water present in the original sample by subtracting the total volume of rinses used from the measured volume of the filtrate.

7.6 Place the following in a 1-liter wide-mouthed bottle:

500 mL water
5 mL 50% w/v NaOH
50 mL n-Hexane (if a heavy grease is present)

If the weight of the solids (Step 7.5) is greater than 25 g, weigh out a representative aliquot of 25 g and add it to the bottle; otherwise add all of the solids. Cap the bottle.

7.7 The pH of the extract must be maintained above 10 throughout the extraction step and subsequent filtration. Since some samples may release acid, the pH must be monitored as follows. Shake the extraction bottle and after one minute, check the pH. If the pH is below 12, add 50% NaOH in 5 mL increments until it is at least 12. Recap the bottle, and repeat the procedure until the pH does not drop.

7.8 Place the bottle or bottles in the tumbler, making sure there is enough foam insulation to cushion the bottle. Turn the tumbler on and allow the extraction to run for about 16 hours.

7.9 Prepare a Buchner funnel apparatus as in Step 7.2 with a glass fiber pad filter.

7.10 Decant the extract to the Buchner funnel. Full recovery of the extract is not necessary.

7.11 If the extract contains an oil phase, separate the aqueous phase using a separatory funnel. Neither the separation nor the filtration are critical, but are necessary to be able to measure the volume of the aliquot of the aqueous extract analyzed. Small amounts of suspended solids and oil emulsions will not interfere.

7.12 At this point, an aliquot of the filtrate of the original sample may be combined with an aliquot of the extract in a proportion representative of the sample. Alternatively, they may be distilled and analyzed separately and concentrations given for each phase. This is described by the following equation:

$$\frac{\text{Liquid Sample Aliquot(mL)}}{\text{Extract Aliquot(mL)}} - \frac{\text{Solid Extracted(g)}^a}{\text{Total Solid(g)}^b} \times \frac{\text{Total Sample Filtrate(mL)}^c}{\text{Total Extraction Fluid(mL)}^d}$$

[a]From Step 7.6. Weight of solid sample used for extraction.

[b]From Step 7.5. Weight of solids and oil phase with the dry weight of filter and tared dish subtracted.

[c]Includes volume of all rinses added to the filtrate (Steps 7.2 and 7.3).

[d]500 mL water plus total volume of NaOH solution. Does not include hexane, which is subsequently removed (Step 7.11).

Alternatively, the aliquots may be distilled and analyzed separately, concentrations for each phase reported separately, and the amounts of each phase present in the sample reported separately.

8.0 QUALITY CONTROL

8.1 Refer to Method 9010.

9.0 METHOD PERFORMANCE

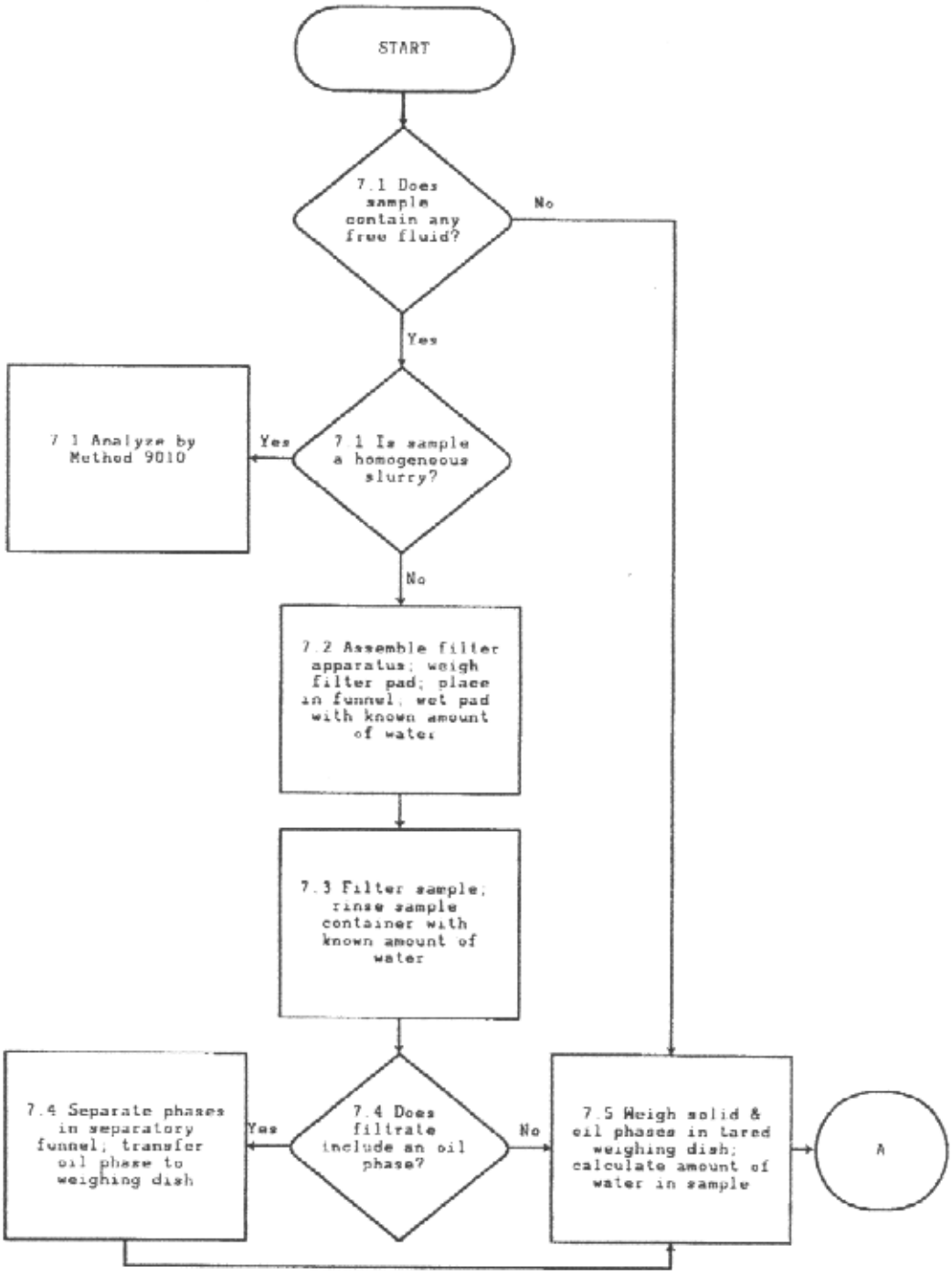
9.1 In a single laboratory study, recoveries of 60 to 90% are reported for solids and 88 to 92% for oils. The reported CVs are less than 13.

10.0 REFERENCES

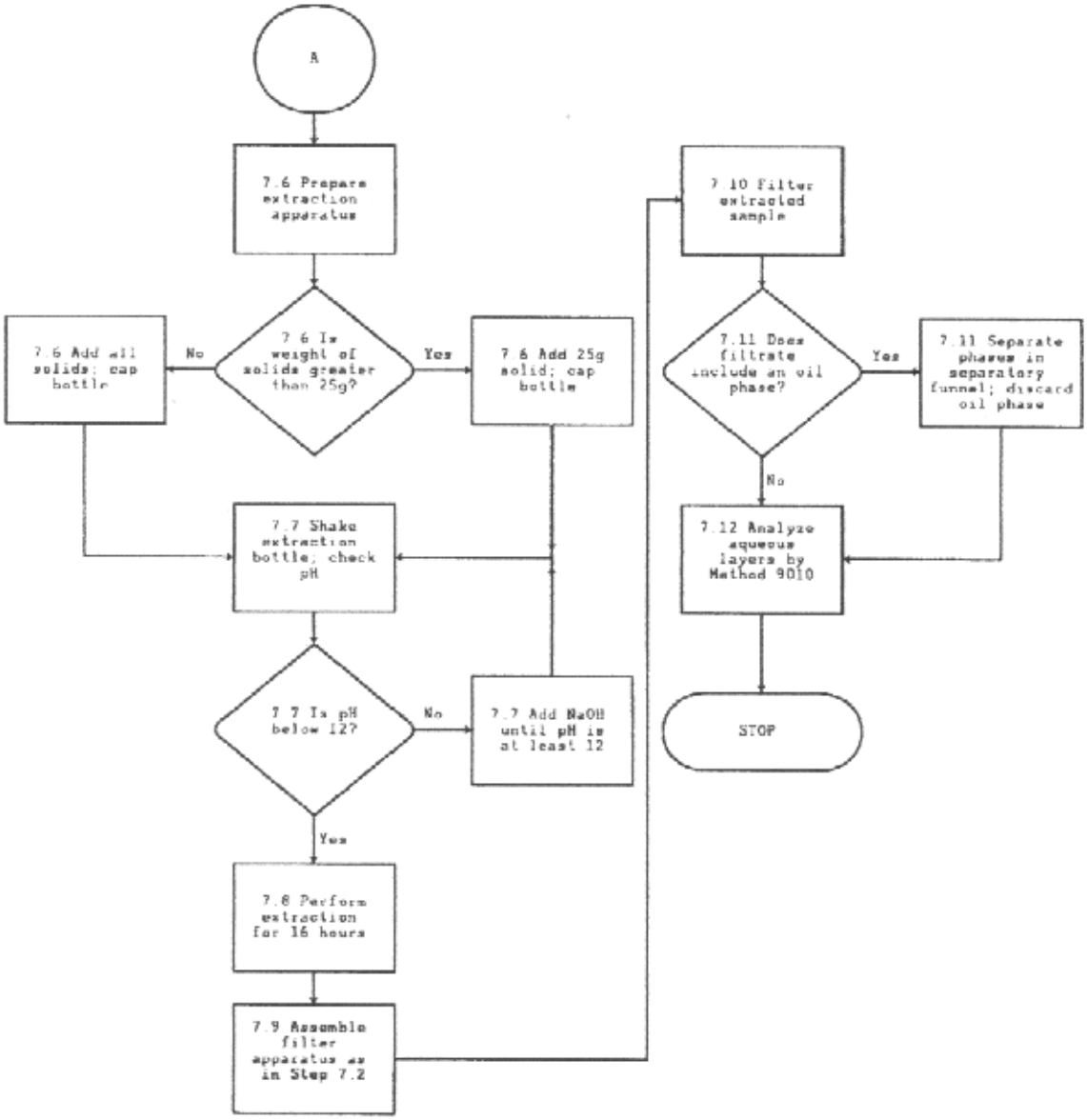
10.1 Refer to Method 9010.

METHOD 9013
(APPENDIX TO METHOD 9010)

CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS



CYANIDE EXTRACTION PROCEDURE FOR SOLIDS AND OILS (CONTINUED)



METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring free (non-complexed) cyanide and hydrocyanic acid in drinking water, natural surface waters, domestic and industrial wastewaters, and in soil extracts. This method may also be used as a determinative step for quantifying total and amenable cyanide in the alkaline distillates from Method 9010.

1.2 The titration procedure using silver nitrate with p-dimethylamino-benzal-rhodanine indicator is used for measuring concentrations of cyanide exceeding 0.1 mg/L (0.025 mg/250 mL of absorbing liquid).

1.3 The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

2.0 SUMMARY OF METHOD

2.1 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl) by reaction of cyanide with chloramine-T at a pH less than 8. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read at 578 nm for the complex formed with pyridine-barbituric acid reagent and CNCl. To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

2.2 The titration measurement uses a standard solution of silver nitrate to titrate cyanide in the presence of a silver sensitive indicator.

3.0 INTERFERENCES

3.1 Interferences are eliminated or reduced by using the distillation procedure provided in Method 9010.

3.2 Refer to Method 9010 for a discussion of potential cyanide interferences.

4.0 APPARATUS AND MATERIALS

4.1 Spectrophotometer - Suitable for measurements at 578 nm with a 1.0 cm cell or larger.

4.2 Hot plate stirrer/heating mantle.

4.3 pH meter.

4.4 Refrigerator.

4.5 5 mL microburette.

4.6 Class A volumetric flasks - 1000, 250, and 100 mL.

4.7 Erlenmeyer flask - 500 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 Reagents for spectrophotometric determination

5.3.1 Sodium hydroxide solution (0.25N), NaOH. Dissolve 10 g NaOH in 1 liter of water.

5.3.2 Sodium phosphate monobasic (1M), $NaH_2PO_4 \cdot H_2O$. Dissolve 138 g of $NaH_2PO_4 \cdot H_2O$ in 1 liter of water. Refrigerate this solution.

5.3.3 Chloramine-T solution (0.44%), $C_7H_7ClNNaO_2S$. Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of water and refrigerate until ready to use.

5.3.4 Pyridine-Barbituric acid reagent, $C_5H_5N \cdot C_4H_4N_2O_3$. Place 15 g of barbituric acid in a 250-mL volumetric flask and add just enough water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of concentrated hydrochloric acid (HCl), mix, and cool to room temperature. Dilute to 250 mL with water. This reagent is stable for approximately six months if stored in a cool, dark place.

5.3.5 Stock potassium cyanide solution (1 mL = 1000 µg CN^-), KCN. Dissolve 2.51 g of KCN and 2 g KOH in 900 mL of water. Standardize with 0.0192N silver nitrate, $AgNO_3$. Dilute to appropriate concentration to achieve 1 mL = 1000 µg of CN^-.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Methods 4500-CN D.

5.3.6 Intermediate standard potassium cyanide solution, (1 mL = 100 µg CN^-), KCN. Dilute 100 mL of stock potassium cyanide solution (1 mL = 1000 µg CN^-) to 1000 mL with water.

5.3.7 Working standard potassium cyanide solution, (1 mL = 10 µg CN^-), KCN. Prepare fresh daily by diluting 100 mL of intermediate standard potassium cyanide solution and 10 mL of 1N NaOH to 1 liter with water.

5.4 Reagents for titration procedure

5.4.1 Rhodanine indicator - Dissolve 20 mg of p-dimethylamino- benzal-rhodanine, $C_{12}H_{12}N_2OS_2$, in 100 mL of acetone.

5.4.2 Standard silver nitrate solution (0.0192N), $AgNO_3$. Prepare by crushing approximately 5 g $AgNO_3$ and drying to constant weight at 40°C. Weigh out 3.2647 g of dried $AgNO_3$. Dissolve in 1 liter of water.

NOTE: Detailed procedure for $AgNO_3$ standardization is described in "Standard Methods for the Examination of Water and Wastewater", 18th Edition, (1992), Method 4500-CN D.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to Method 9010 for guidance on sample collection, preservation, and handling.

6.2 Distillates that are not analyzed immediately should be stored in tightly sealed flasks at 4 °C.

7.0 PROCEDURE

7.1 If the manual spectrophotometric determination will be performed, proceed to Section 7.2. If the titration procedure will be performed, proceed to Section 7.6.

7.2 Manual spectrophotometric determination

7.2.1 Pipet 50 mL of sample or 50 mL of the scrubber solution obtained from the distillation procedure in Method 9010 into a 100-mL volumetric flask. If the sample is later found to be beyond the linear range of the colorimetric determination and redistillation of a smaller sample is not feasible, a smaller aliquot may be taken. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution.

NOTE: Temperature of reagents and spiking solution can affect the response factor of the colorimetric determination. The reagents stored in the refrigerator should be warmed to ambient temperature before use. Samples should not be left in a warm instrument to develop color, but instead they should be aliquoted to a cuvette immediately prior to reading the absorbance.

7.2.2 Add 15 mL of 1M sodium phosphate solution and mix. Add 2 mL of chloramine-T and mix. Some distillates may contain compounds that have chlorine demand. One minute after the addition of chloramine-T, test for excess chlorine with KI-starch paper. If the test is negative, add 0.5 mL chloramine-T. After one minute recheck with KI-starch paper. Continue to add chloramine-T in 0.5 mL increments until an excess is maintained. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution and mix.

7.2.3 Dilute to 100 mL with water and mix again. Allow 8 minutes for color development and then read the absorbance at 578 nm in a 1-cm cell within 15 minutes. The sodium hydroxide concentration will be 0.125N.

7.3 Standard curve for samples without sulfide

7.3.1 Prepare a series of standards by pipetting suitable volumes of working standard potassium cyanide solution into 250-mL volumetric flasks. To each flask, add 50 mL of 1.25N sodium hydroxide and dilute to 250 mL with water. Prepare using the following table. The sodium hydroxide concentration will be 0.25N.

mL of Working Standard Solution (1 mL = 10 µg CN^-)	Concentration (µg CN^-/L)
0	Blank
1.0	40
2.0	80
5.0	200
10.0	400
15.0	600
20.0	800

7.3.2 After the standard solutions have been prepared according to the table above, pipet 50 mL of each standard solution into a 100-mL volumetric flask and proceed to Sections 7.2.2 and 7.2.3 to obtain absorbance values for the standard curve. The final concentrations for the standard curve will be one half of the amounts in the above table (final concentrations ranging from 20 to 400 µg/L).

7.3.3 Prepare a standard curve ranging from 20 to 400 µg/L by plotting absorbance of standard versus the cyanide concentration

7.4 Standard curve for samples with sulfide

7.4.1 It is imperative that all standards be distilled in the same manner as the samples using the method of standard additions. Standards distilled by this method will give a linear curve, at low concentrations, but as the concentration increases, the recovery decreases. It is recommended that at least five standards be distilled.

7.4.2 Prepare a series of standards similar in concentration to those mentioned in Section 7.3.1 and analyze as in Section 7.2. Prepare a standard curve by plotting absorbance of standard versus the cyanide concentration.

7.5 Calculation - If the spectrophotometric procedure is used, calculate the cyanide, in µg/L, in the original sample as follows.

$$CN^- \text{ (µg/L)} = \frac{A \times B \times C}{D \times E}$$

where:

A = µg/L CN^- read from standard curve.
B = mL of sample after preparation of colorimetric analysis (100 mL recommended).

C = mL of sample after distillation (250 mL recommended).
D = mL of original sample for distillation (500 mL recommended).
E = mL used for colorimetric analysis (50 mL recommended).

7.6 Titration Procedure

7.6.1 Transfer the gas scrubber solution or a suitable aliquot from the 250-mL volumetric flask to a 500-mL Erlenmeyer flask. Add 10-12 drops of the rhodanine indicator.

7.6.2 Titrate with standard 0.0192N silver nitrate to the first change in color from yellow to brownish-pink. The titration must be performed slowly with constant stirring. Titrate a water blank using the same amount of sodium hydroxide and indicator as in the sample. The analyst should be familiar with the endpoint of the titration and the amount of indicator to be used before actually titrating the samples. A 5-mL buret may be conveniently used to obtain a precise titration.

NOTE: The titration is based on the following reaction:

$$Ag^{+} + 2CN^{-} \rightarrow [Ag(CN)_2]^{-}$$

When all of the cyanide has complexed and more silver nitrate is added, the excess silver combines with the rhodanine indicator to turn the solution yellow and then brownish-pink.

7.6.3 Calculation - If the titrimetric procedure is used, calculate concentration of CN^- in µg/L in the original sample as follows:

$$CN^{-}(\mu g/L) = \frac{(A-B)}{C} \times D \times \frac{E}{F} \times \frac{2\ mole\ CN^{-}}{1\ eq.\ AgNO_3} \times \frac{26.02\ g\ CN^{-}}{1\ mole\ CN^{-}} \times \frac{1 \times 10^{6} \mu g}{1\ g}$$

where:

A = mL of $AgNO_3$ for titration of sample.
B = mL of $AgNO_3$ for titration of blank.
C = mL of sample titrated (250 recommended).
D = actual normality of $AgNO_3$ (0.0192N recommended).
E = mL of sample after distillation (250 recommended).
F = mL of original sample before distillation (500 recommended).

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference or inspection.

8.2 Refer to the quality control section of Method 9010A for the method requirements for blanks, matrix duplicates, and matrix spikes. Each QC sample must be processed through the reflux-distillation steps contained in Method 9010 prior to analysis by this method.

8.3 Analyze check standards with every analytical batch of samples. If the standards are not within 15% of the expected value, then the samples must be reanalyzed.

8.4 Analyze one replicate sample for every 20 samples. The CV of the replicates should be 20% or less. If this criterion is not met, the samples should be reanalyzed.

8.5 Analyze one matrix spiked sample every 20 samples to check the efficiency of sample distillation procedure and to monitor potential matrix interference.

8.6 The method of standard additions shall be used for the analysis of all samples that suffer from matrix interferences such as samples which contain sulfides.

9.0 METHOD PERFORMANCE

9.1 The titration procedure using silver nitrate is used for measuring concentrations of cyanide exceeding 0.1 mg/L. The colorimetric procedure is used for concentrations below 1 mg/L of cyanide and is sensitive to about 0.02 mg/L.

9.2 EPA Method 335.2 (sample distillation with titration) reports that in a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.06 to 0.62 mg/L CN^-, the standard deviations for precision were $\pm$ 0.005 to $\pm$ 0.094, respectively. In a single laboratory using mixed industrial and domestic waste samples at concentrations of 0.28 and 0.62 mg/L CN^-, recoveries (accuracy) were 85% and 102%, respectively.

9.3 In two additional studies using surface water, ground water, and landfill leachate samples, the titration procedure was further evaluated. The concentration range used in these studies was 0.5 to 10 mg/L cyanide. The detection limit was found to be 0.2 mg/L for both total and amenable cyanide determinations. The precision (CV) was 6.9 and 2.6 for total cyanide determinations and 18.6 and 9.1 for amenable cyanide determinations. The mean recoveries were 94% and 98.9% for total cyanide, and 86.7% and 97.4% for amenable cyanide.

10.0 REFERENCES

10.1 Refer to Method 9010 for references on total and amenable cyanide.

METHOD 9014

TITRIMETRIC AND MANUAL SPECTROPHOTOMETRIC DETERMINATIVE METHODS FOR CYANIDE